

# A method to simultaneously determine reduction in PAH dissolved concentrations and bioaccessibility in carbon amended soils

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Carbon amendments are being studied to be used as an *in-situ* remediation method for contaminated sediments. Most studies have focused on the efficiency of the added amendments to reduce the availability of the chemical contaminants. Fewer studies have been directed to follow the potential adverse effects of these amendments. The contaminated sites may have viable benthic community and therefore remediation actions can disturb the ecosystem. On the other hand, bioaccumulation in the food web results in a situation where the organisms in the higher trophic levels are at risk and/or they cannot be used for human consumption, which increases the remediation pressures. In order to find the best method for remediation the potential adverse effects of restoration measures needs to be evaluated. In this study, we assessed the effects of activated carbon and biochar in PCB contaminated sediments on feeding, growth and reproduction of an experimental organism *Lumbriculus variegatus*. We used coal based activated carbon and wood based biochar, which we mixed in separate experiments to the sediments. In addition, we tested if cleaning (hot water, solvent extraction) of activated carbon would affect the measured parameters. Activated carbon had sediment specific adverse effects on feeding and growth. The adverse effects of biochar were minor than those observed with comparable doses of activated carbon. The pre-treatment of the activated carbon by hot water or solvent extraction had only minor effects on the measured biological parameters. The ecological consequences inflicted by carbon amendments should be considered sediment specifically.

**TUPC4-4**
**Bioavailability reduction with activated carbon amendment: comparison of field results and expectations under optimal conditions**
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Application of activated carbon (AC) at the pilot-scale in Grasse River, NY USA has been shown to reduce the potential human and ecological health risks posed by polychlorinated biphenyl (PCB)-impacted sediment by reducing bioavailability. For instance, over 3-years of post-application monitoring, bioaccumulation in a freshwater oligochaete worm was reduced by 62 - 99% compared to untreated background sediment, and pore water concentrations measured by an aqueous equilibrium batch test were reduced by >93%. To provide perspective on how the level of reductions achieved in the field relate to the reductions that may be expected under optimal conditions, PCB bioaccumulation in L. variegatus from mixed tiller field-amended sediments was compared to exposures where AC was first preloaded with a mixture of PCBs (Aroclor 1260). In addition, aqueous equilibrium measurements were compared to modeled pore water concentrations assuming equilibrium conditions with a range of AC doses according to a dual-sorption model which was parameterized for the organic carbon and activated carbon present in Grasse River sediment. When PCBs were preloaded on AC and amended to clean sediment, the bioaccumulation observed in L. variegatus was 93% less for total PCBs compared to spiked unamended sediment, with bioaccumulation of tetra and penta chlorobiphenyls less by 98 and 96%, respectively. When results are compared for a tetra and penta PCB congener which are at similar concentrations in the spiked and field sediments it is evident that bioaccumulation is greatly reduced with field-aged AC amendment but not to the level achieved when the majority of PCBs have been transferred to the AC. Aqueous pore water concentrations modeled at equilibrium were 1-2 orders of magnitude lower than the aqueous equilibrium batch test results. This large apparent difference is partly accentuated by the fact that several measurements were below detection limits and may lie closer to predictions. These results indicate that optimum equilibrium sorption has not been achieved in the field, likely as a result of the combination of relatively slow mass transfer kinetics and sorption attenuation of PCBs in the field by natural organic matter. This field study has shown AC amendment to be effective at reducing bioavailability of PCBs in sediment, but that longer periods of time will be necessary to allow sequestration of PCBs by AC to reach its full potential.

**TUPC4-5**
**Use of bioadsorbents to reduce the leaching in soil of fluometuron and MCPA**
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The environmental impact of herbicides, especially their presence in surface and ground waters, can be minimized in a preventive way with the use of controlled release formulations and in a corrective way with the use of barriers or filters that trap and immobilize them. For both applications, materials such as natural clays, anionic or modified, and other bioadsorbents coming from natural wastes have shown their utility. Among the bioadsorbents there is a great interest in biochar (solid residue produced by biomass pyrolysis) as a soil amendment, because it is a stable source of nutrients, and its contribution to carbon sequestration. Due to the important role of the solid natural or added soil components on the processes related to the presence of herbicides in water, it is interesting to compare the effects of biochar to those of organoclays. The aim of this work was to compare the effect of an organoclay saturated with hexadecylthrimethylammonium (SAz-HDTM) cation and three biochars used as a soil amendment (2% w/w) on the adsorption and mobility of the herbicides fluometuron (N,N-dimethyl-N"-[3-(trifluoromethyl)phenyl]urea) and MCPA (4-chloro-2-methyl phenoxyacetic acid). Results showed that all adsorbents increased the adsorption of both herbicides on the soil, decreasing their leaching or percolation losses, except for biochar (BC2). The lower adsorption and higher leaching of both herbicides observed in the soil amended with BC2 is due to the high content on dissolved organic matter (DOM) of the biochar, which probably compete with the herbicides for the adsorption sites and/or the formation of one DOM-herbicide complex with higher water solubility, facilitating its mobility with water. The other biochars are efficient in decreasing the herbicides´ percolation by 50-70% for fluometuron and 30% for MCPA. For both herbicides, the organoclay is less efficient as compared to the biochars, decreasing the percolation of fluometuron by 35% and MCPA by 45%. The reduction is directly proportional to the adsorption capacity of this organoclay for both herbicides and is related to the interactions organoclay-herbicides at molecular level, due to the neutral character of fluometuron and acidic character of MCPA. These interactions are also shown by the movement of the peak of maximum concentration of the breakthrough curves in the soils amended as compared to the unamended soil.

**TUPC4-6**
**A method to simultaneously determine reduction in PAH dissolved concentrations and bioaccessibility in carbon amended soils**
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Soils polluted with polyaromatic hydrocarbons (PAHs) represent a risk to the environment. Therefore, different soil amendments including activated charcoal (AC), biochar (charcoal) and compost are often added to remediate such soils. On the one hand, this leads to a reduction in the PAH dissolved concentrations, and therefore also bioconcentration and toxicity. On the other hand, strong sorption to the soil amendments can reduce bioaccessibility to degrading microorganisms, decreasing the efficiency of remediation. Therefore, to understand the effects of soil amendment addition, methods are needed that can simultaneously determine both the changes in PAH dissolved concentrations and their bioaccessibility. In this study an approach based on the sequential sorption of phenanthrene (Phe), as a model PAH, into an infinite sink consisting of silicone O-rings was developed. The extent of abiotic desorption ($t$ = 24 d) of [9-$^{14}$C]Phe from suspensions made up of sandy loam soil (either Outfield, RS, or Olsen) plus amendment (either AC, charcoal, or compost) was investigated. The total amount of Phe desorbed was 6 to 10% for AC, 38 to 44% for charcoal, 87 to 106% for compost, and 95 to 106% for the control without any soil amendment. The temporal development in desorption was accompanied by a parallel decrease in the Phe dissolved concentration. Desorption was then compared to the extent of mineralization ($t$ = 15 d) of Phe sorbed to the soil plus amendment suspensions by *Sphingomonas sp* (DSM 12247). Between the different soils and amendments, desorption and mineralization followed the same trends, but mineralization was slightly lower with the peak of Phe mineralization correlated with a peak in bacterial growth. Interestingly, compost induced a higher cell density but inhibited the Phe mineralization. Therefore, desorption of Phe into an infinite silicone sink was a useful tool for predicting the extent of mineralization (bioaccessibility) as well as changes in dissolved concentrations. Furthermore, the silicone O-ring format used in this study was practical to handle and greatly simplified the final Phe analyses.

**TUPC4-7**
**Impact of wood biochar on the biodegradation and bioavailability of naphthalene in soil**
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Naphthalene is a major component of naturally occurring coal tar and crude oil. It can however be volatilized or biodegraded efficiently in soil but at high concentrations it could leach to aquatic systems and express toxicity to aquatic life. In order to enhance remediation of naphthalene, biochar, which is a carbon rich product from the pyrolysis of biomass can be utilised to control its fate in the environment. This study investigated the influence of 0%, 0.1%, 0.5% and 1.0% of two different biochar (BC1 and BC2) sourced from wood wastes on the relationship between microbial mineralisation and hydroxypropyl-β-cyclodextrin (HPCD), $CaCl_2$ and methanol extractions of $^{14}$C-naphthalene (50 mg kg$^{-1}$) in soil. BC1 was produced at 450$^{o}$C for 16 hours and BC2 was produced at 1000$^{o}$C for 1 hour. The amendment conditions were aged for 0, 18, 36 and 72 days. The total extent of $^{14}$C-naphthalene mineralisation was assessed by monitoring $^{14}$C-naphthaene mineralisation over 14 days in respirometric assays using indigenous microflora and compared to HPCD, $CaCl_2$ and methanol extractions. Results showed that the 0.5 and 1.0% of BC1 and all concentrations of BC2 amendments showed significant reduction ($p < 0.01$) in extent of mineralisation compared to 0% BC and cumulative extractions. Linear correlation between HPCD extractability and total amount mineralised over 14 days revealed very good correlation in all concentrations of biochar amendments BC1 ($r^2$ = 0.94, slope = 0.94, intercept = -0.86) and BC2 ($r^2$ = 0.94, slope = 0.90, intercept = -1.34). However, fastest rate of mineralisation showed poor correlation. Additionally, the $CaCl_2$ and methanol extractions underestimated and overestimated extent of mineralisation respectively. Bioaccessibility often describes the biodegradation endpoint. This paper thus states that biochar used in this study can reduce the bioaccessibility of naphthalene at high concentrations and that HPCD extraction strongly predicts the bioaccessibility of naphthalene in soils even when amended with biochar. However, the production process, feedstock and soil properties determine the capability of biochar to adsorb organic contaminants.

**TUPC4-8**
**Status on activated carbon amendments to reduce bioaccumulation and possible secondary effects**
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Innovative in-situ remediation techniques are being investigated to reduce the release and bio-uptake of contaminants from sediments polluted with hydrophobic organic compounds (HOCs) [1]. Sediment amendments with a strong sorbent material like activated carbon (AC) is one alternative in-situ approach for remediation based on the